"A direct-alcohol fuel-cell and corresponding method of fabrication"

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BACKGROUND OF THE INVENTION

The present invention relates to a direct-alcohol fuel-cell stack.

Fuel cells are electrochemical devices capable of converting the chemical energy contained in a fuel into electrical direct current, in the absence of moving parts.

Said electrochemical device comprises an anode and a cathode separated by an electrolyte, i.e., a substance that enables migration of the ions. In order to favour the electrochemical reactions it is necessary to use appropriate catalysts, for example platinum.

The cell is supplied with the fuel (typically hydrogen or another molecule containing hydrogen) and with an oxidant (typically oxygen or air), which, electrochemically combined, generate electricity and produce water as waste product.

The individual cells, characterized by voltages comprised between half a volt and one volt according to the technology adopted, can be connected in series, so as to obtain a total voltage of the desired value. Said arrangement of the cells forms the so-called *fuel-cell stack*, to which there can be associated an inverter and a transformer for converting the direct current generated by the stack of cells into alternating current at the desired voltage and at the desired frequency.

Development of fuel cells and of their applications is currently retarded to a large extent by the production costs involved, which are still high, and by certain technological and manufacturing problems.

In this perspective, it should for example be noted

that the traditional systems of production of electrode structures for fuel cells are based upon the deposition of catalysts on carbon substrates, hot-pressed on an electrolyte in the form of a membrane. The said technique has proven costly.

Current fuel cells suffer, moreover, from a certain slowness of operation in the step of start-up of the electrochemical process, and this precludes their use in those applications that entail an immediate generation of electrical energy.

SUMMARY OF THE INVENTION

The purpose of the present invention is to provide a newly conceived fuel cell, of particularly advantageous use from the cost point of view and/or from the functional point of view for the purposes of production of fuel-cell usable as independent systems for the production of energy.

This and other purposes are achieved, according to the present invention, by a fuel-cell which has direct-alcohol fuel cells having a structure which comprises:

- a first electrode;
- a second electrode;
- an electrolyte arranged between the first electrode and the second electrode;
- means for conducting electrical current to the first electrode; and
- means for conducting electrical current to the second electrode,

where said structure is miniaturized, made up of a plurality of layers set on top of one another and associated in an unremovable way to a flexible substrate.

Preferred embodiments of the fuel-cell according to the invention and of its method of fabrication are specified in the attached claims, which are understood

as forming an integral part of the present description.

BRIEF DESCRIPTION OF THE DRAWINGS

Further purposes, characteristics and advantages of the present invention will emerge clearly from the description that follows with reference to the annexed drawings, which are provided purely by way of non-limiting example and in which:

- Figure 1 is a schematic illustration of the structure of a direct-methanol fuel cell;
- Figure 2 is a schematic illustration of a miniaturized fuel-cell obtained in accordance with the present invention; and
- Figure 3 represents a schematic cross-sectional view of a miniaturized fuel cell obtained according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

As mentioned in the introductory part of the present description, a fuel cell is a system consisting of two electrodes (an anode and a cathode), between which is set an electrolyte, usually in the form of a membrane, which directly converts chemical energy into electrical energy, without combustion or moving parts, by means of the electrochemical combination of hydrogen and oxygen, producing water, electricity and heat.

Methanol has proven one of the best candidates as fuel for fuel cells, on account of its ease of storage and transportation and its low cost. The use of methanol in liquid form enables a considerable reduction of the complexity of the fuel cells, enabling their application in various sectors. It should moreover be noted that in the case of cells which use methanol in aqueous solution, known as direct-methanol fuel cells (DMFCs), the fuel can be supplied in the absence of preliminary *reforming*, i.e., a treatment to which fuels rich in hydrocarbons must, instead, be subjected for

converting them into hydrogen.

Figure 1 is a schematic representation of the typical structure of a fuel cell which uses methanol in aqueous solution ($CH_3OH + H_2O$) as source of hydrogen.

In said figure, FC designates the cell as a whole, which comprises an anode 2 and a cathode 3, between which is set a suitable membrane 4, which has the function of electrolyte.

The electrodes 2 and 3 can each be formed by applying on the opposite faces of the membrane 4 a thin catalytic layer, consisting of granules of carbon activated with noble metals and carrying PTFE or Teflon™, for impermeabilization of some pores.

The cell FC moreover envisages two bipolar plates that are located on both sides of the membrane 4 and are provided for enabling passage of electrical current and for yielding heat to the external environment.

The reference numbers 5 and 6 designate, respectively, an inlet of the fuel in a chamber of the anode 2 and an outlet from said chamber for the carbon dioxide produced by the electrochemical reaction. The numbers 7 and 8 designate, respectively, an inlet for air into a chamber of the cathode 3 and an outlet from said chamber for the water produced by the electrochemical reaction.

In a cell of the type illustrated in Figure 1, the alcohol laps the anode 2, whilst the oxidant laps the cathode 3. The catalytic layer of the anode 2 stimulates the electro-oxidation of the molecules of alcohol, which separate into positive ions and electrons. Whilst the electrons pass from the anode 2 to the cathode 3 through the electrical load, the protons migrate from the anode 2 to the cathode 3 through the membrane 4 and, once they have reached the cathode 3, combine with the oxygen in the air and with

the electrons that come from the anode 2, to form water.

In other words, then, the water-methanol mixture is sent directly to the anode 2, by means of the inlet 5, where it reacts, releasing CO_2, H^+ ions, and electrons. By means of the inlet 7, the air is, instead, carried to the cathode 3, the O_2 of which reacts with the H^+ ions diffused through the membrane 4 and with the electrons, to be reduced to H_2O.

The cell reactions at the anode 2 and at the cathode 3 are, respectively, the following:

$$\mathbf{CH_3OH + H_2O \rightarrow 6e^- + 6H^+ + CO_2}$$

$$\mathbf{3/2O_2 + 6e^- + 6H^+ \rightarrow 3H_2O}$$

which, combined, yield the overall reaction:

$$\mathbf{CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2}$$

There may thus be noted the transport of three different species:

- the electrons move through the carbon of the electrode/catalyst;
- the gases diffuse through the impermeabilized pores of the electrode layer, which, as has been said, consists of granules of carbon activated with noble metals and carrying PTFE or Teflon™ for impermeabilization of some pores;
- the liquid water flows through the non-impermeabilized pores.

According to a first important aspect of the invention, it is proposed to provide a new miniaturized structure of fuel cell of the type mentioned above, made up of more than one layers of different materials on a flexible support.

Figure 2 is a schematic representation of a miniaturized direct-alcohol fuel-cell stack according to the invention, designated as a whole by 20.

The fuel-cell stack 20 has a control portion 20A and a

portion for generation of energy 20B.

The portion 20B comprises a flexible support designated by 21, which in the case exemplified is in the form of a film made of polymeric material. By way of example, a material usable for the fabrication of the supporting film 21 is Kapton®, a light, insulating, polyamide material, which presents excellent resistance to heat, good thermal conductivity and is non-absorbent.

Provided on the film 21 are a plurality of miniaturized direct-methanol fuel cells, designated by FC, each provided with an inlet 22 for the fuel and an outlet 23 for the water resulting from the chemical reaction.

The reference number 24 designates a duct for supply of the methanol-based fuel, from which there branch off the inlets 22. The number 25 designates a duct for discharge of the water generated by the cells FC, from which there branch off the outlets 23.

The fuel-distribution system, formed by the duct 24 and by the inlets 22, and the water-discharge system, formed by the duct 25 and by the inlets 23, can be obtained by hot-pressing of a polymeric layer on the supporting film 21.

The reference number 26 designates conducting paths that connect the cells FC in series to one another; said connections can be obtained by means of deposition of electrically conductive material on the supporting film 21.

The control module 20A comprises a micro-pump 30, preferably of a piezoelectric type and made using MEMS (*Micro Electro-Mechanical Systems*) technology, which has the function of regulating the supply of fuel to the various cells FC. For this purpose, the micro-pump 30 comprises a respective inlet branch 30A, for connection to the source of methanol in aqueous solution, and a delivery branch 30B, provided for being

hydraulically connected, with modalities in themselves known, *to the duct 24 of the portion 20B.*

The micro-pump 30 has also the important function of maintaining the cell FC moist, when this is not in use, with the aim of preventing the deterioration of its electrode-electrolyte structure.

The micro-pump 30 is controlled by a microprocessor designated by MP, which likewise controls a supercapacitor, designated by 31. The supercapacitor 31 is of a conception in itself known and consequently will not be described herein; here it will suffice to recall that a supercapacitor is an electronic device, obtainable using nanotechnologies, which is capable of accumulating static electricity and supplying electrical energy and is made up of two polarizable electrodes, a separator, and an electrolyte, where the electric field is stored in the interfaces between the electrolyte and the electrodes.

In the application herein proposed, the supercapacitor 31 is provided for being electrically connected, with *modalities in themselves known, to the paths 26 at* input to the first cell FC of the portion 20B. Its function is that of compensating the time of response of the electrochemical system and activating the electrical load supplied by the *fuel-cell stack 20* before this can achieve the maximum electrical output to the output 26A of the paths 26. The first cell FC of the portion 20B of the fuel-cell stack, as in a loop, functions then as charger of the supercapacitor 31, when the electrical load does not absorb current.

A further function of the supercapacitor 31 is that of supplying the microprocessor MP, and thus also the micro-pump 30.

As mentioned previously, traditional systems of production of the electrode structures for fuel cells

are based upon the deposition of catalysts on carbon substrates, hot-pressed on the electrolyte, i.e., the membrane.

According to the present invention, there is instead proposed recourse to micromachining to obtain multiple layers that form the components of the cells FC on the substrate made from the film 21, with a technique similar to the one currently in use for the production of various printed circuits.

Figure 3 shows the multi-layer structure of an individual miniaturized cell FC provided according to the invention, which can be obtained with various procedures.

In a first possible implementation, on the flexible supporting film 21 there are defined the paths 26, by means of deposition of electrically conductive material. The supporting film 21 is then provided with the fuel-distribution system 22, 24 and the water-discharge system 23, 25, for example by means of hot-pressing of a polymeric layer on the film itself.

Subsequently, in an area corresponding to the area in which a cell FC is to be obtained, deposited on the film 21 is a layer of metallic coating, designated in Figure 3 by RMI. On the layer RMI there is then positioned an electrode-electrolyte assembled structure, which comprises:

- an appropriate anodic catalyst, designated by CA, which functions as positive electrode;
- an appropriate cathodic catalyst, designated by CC, which functions as negative electrode; and
- a suitable electrolyte EL, set between the anodic catalyst CA and the cathodic catalyst CC.

Following upon positioning of the aforesaid assembled structure, on the cathodic catalyst, there is deposited a layer of metallic coating RMS. Possibly deposited on

the latter is, finally, a protective layer made of polymeric material RP.

As an alternative to the technique described herein, the electrode-electrolyte structure could be obtained by depositing the anodic catalyst CA on the layer RMI. On the anodic catalyst CA there will then be positioned or deposited the electrolyte EL. This will be followed, in order, by deposition of the cathodic catalyst CA, of the layer of metallic coating RMS, and of the possible protective layer RP.

Another possibility is that of obtaining separately the complex formed by the layers RMI, CA, EL, CC, RMS, then to proceed to its fixing (for example, by gluing) on the flexible supporting film 21.

Operation of the miniaturized cells FC forming part of the fuel-cell stack illustrated in Figure 2 is similar to the one described previously with reference to Figure 1. It is to be noted, in this connection, that the metallic layers RMI and RMS provide means for conducting the electrical current to the electrodes CA, CC.

The electrodes or catalysts CA, CC may comprise granules of carbon and a noble metal, such as for example platinum, palladium, rhodium, iridium, osmium or ruthenium, and the electrolyte EL can be in the form of a membrane of Naphion.

In a preferred embodiment, it is possible to envisage deposition of the catalysts CA, CC on zeolite materials, with the aim of increasing the catalytic activity. The electrolyte EL may thus advantageously be in the form of a composite Naphion-zeolite membrane, in order to enable reduction of the *cross-over* of methanol.

Once again in order to increase the catalytic activity, in an advantageous variant embodiment, the catalysts

CA, CC can comprise fullerenes and/or carbon nanotubes and/or carbon nanofibres.

From what has been described previously, it is clear how the cells FC are supported by a polymeric film 21, giving rise to an overall flexible structure that may present a considerable development in length.

In effect, the said structure is thus configured as a continuous ribbon having a thickness of some millimetres, which can be rolled up. From said ribbon it will be possible to cut a piece designed to form the portion 20B illustrated in Figure 2, comprising a desired number of cells FC according to the total voltage that it is intended to reach. To this piece there will evidently be combined the respective control portion 20A.

The use of micromachining for obtaining multiple layers that form the components of the cells FC on the flexible substrate made from the film 21 enables, according to the invention, production of low-cost fuel-cell stacks with high production volumes.

Of course, without prejudice to the principle of the invention, the details of construction and the embodiments may vary with respect to what is described and illustrated herein purely by way of example.

It is to be pointed out, in particular, that the structure described is applicable also to the production of other types of direct-alcohol fuel cells, i.e., designed for being supplied with ethanol or other alcohols different from methanol.